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HIGH-TEMPERATURE INTERACTION BETWEEN CALCIUM AND STRONTIUM TITANODISILICATES

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High-temperature interactions between the calcium and strontium titanodisilicates were studied. It was determined that two limited series of solid solutions in the tetragonal system based on these initial compounds are formed. It was found that the changes in the physical-chemical properties of the solid solutions are discontinuous functions of solution composition. Glasses and glass ceramic materials based on the experimental system $Ca_2TiSi_2O_8$ – $Sr_2TiSi_2O_8$ were obtained and the characteristic features of the crystallization of glass and the temperature range of the existence of the crystalline phase were determined.

Key words: high-temperature interaction, titanodisilicates, calcium, strontium, solid solutions, limited solid solutions, glasses, glass ceramic materials.

It is known that glasses and glass ceramic materials based on titanosilicates of alkali-earth metals are used successfully in the production of different glasses, glazes, enamels, and pyroceramics. In this connection the purposeful synthesis and production of these materials can be accomplished only on the basis of a complete understanding of the physical–chemical processes occurring during the reactions in the solid state and crystallization of glasses and metals.

The published information on the reactions leading to the formation of ternary compounds of titanosilicates of alkali-earth metals is limited, and there is no published information on the kinetics and mechanisms of the formation of such compounds. Essentially, the studies are concerned only with obtaining calcium, barium, and strontium titanosilicates and not with the complex processes associated with the formation and recrystallization of stable phases [1 – 4].

To work out rational regimes for the synthesis of titanosilicates of alkali-earth metals it is necessary to study the process leading to their formation in a wide temperature range.

This article presents the results of an investigation of the high-temperature chemical interaction between calcium titanodisilicates ($Ca_2TiSi_2O_8$) and strontium titanodisilicates ($Sr_2TiSi_2O_8$). The system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$ was studied by means of x-ray diffraction, crystal-optics, IR-spectroscopic, and electron-microscopic analyses.6

The compounds $Ca_2TiSi_2O_8$ and $Sr_2TiSi_2O_8$ synthesized from oxide compounds by the solid-phase method of sintering served as the initial materials for synthesizing the solid solutions.

The crystal-optical studies performed by the immersion method [5] using a MIN-8 microscope showed that the refractive indices of the crystals are as follows: $N_g = 2.051$, $N_p = 1.962$ for $Ca_2TiSi_2O_8$; $N_g = 1.764$, $N_p = 1.730$ for $Sr_2TiSi_2O_8$; density at 20°C 3110 kg/m^3 for $Ca_2TiSi_2O_8$ and 3723 kg/m^3 for $Sr_2TiSi_2O_8$.

X-ray diffraction analysis showed that both compounds — calcium titanodisilicate and strontium titanodisilicate, forming the binary system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$, are isostructural and crystallize in the tetragonal system with the following unit-cell parameters: $a = 0.838$ nm, $c = 0.534$ nm for $Ca_2TiSi_2O_8$ and $a = 0.852$ nm, $c = 0.493$ nm for $Sr_2TiSi_2O_8$.

According to the notions of isomorphism of crystal-chemical structures, if in a two-component or binary system the extreme terms of the system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$, i.e., the initial components, crystallize in the same system of crystal structures, then continuous solid solutions based on these compounds can be expected to form during high-tem-

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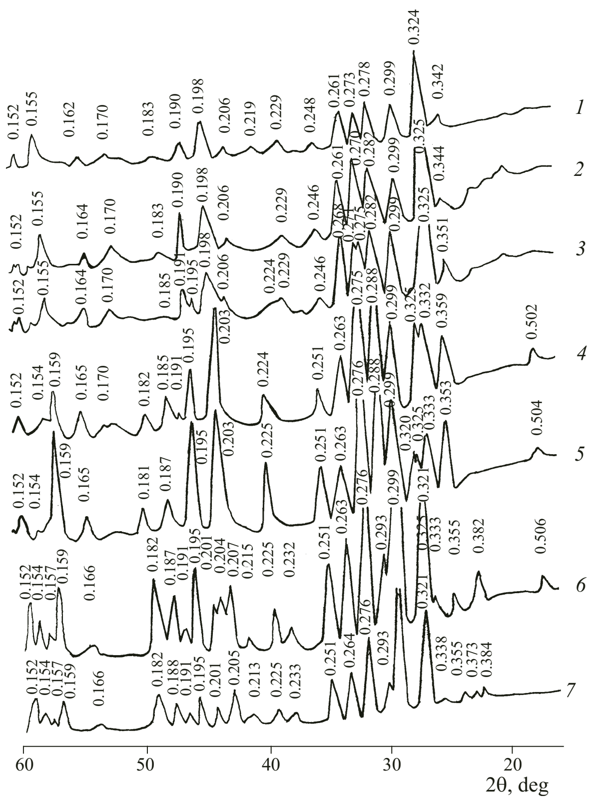

Fig. 1. Diffraction patterns of the solid solutions of the system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$: *1*) $Ca_2TiSi_2O_8$; *2*) $Ca_{1.8}Sr_{0.2}TiSi_2O_8$; *3*) $Ca_{1.2}Sr_{0.8}TiSi_2O_8$; *4*) $Ca_{1.0}Sr_{1.0}TiSi_2O_8$; *5*) $Ca_{0.6}Sr_{1.4}TiSi_2O_8$; *6*) $Ca_{0.2}Sr_{1.8}TiSi_2O_8$; *7*) $Sr_2TiSi_2O_8$.

perature interaction. It was determined on the basis of experimental data that the extreme terms of the system are isostructural and therefore it can be supposed that solid solutions of the same type are formed.

Microstructural studies showed that the microstructures of samples of the experimental system after sintering at 1300°C for 5 h contain uniform, needled-shaped, birefringent crystals.

The results obtained for the refractive indices, density, unit-cell parameters, linear thermal expansion coefficient, and the melting temperatures of the solid solutions as a function of the composition are presented in Table 1. It is evident that the character of the changes in these properties indicates the presence of three regions in the experimental system: the region of the solid solution based on $Ca_2TiSi_2O_8$, the region of the solid solution based on $Sr_2TiSi_2O_8$, and the region where these solid solutions coexist.

A detailed analysis of the splitting and changes of the intensities of individual lines in the diffraction patterns of the samples of the system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$ (Fig. 1) also makes it possible to identify two types of solid solutions in this system.

For samples of this binary system with molar content 10, 20% $Ca_2TiSi_2O_8$ an even variation of the interplanar distances and their line intensities is observed in the x-ray diffraction patterns. This also holds for samples with molar content 10, 20% $Sr_2TiSi_2O_8$.

In the x-ray diffraction pattern of a sample with 30% dicalcium titanodisilicate a sharp increase in seen in the intensity of the line with interplanar distance 0.293; in addition, the splittings 0.207 and 0.204 nm appear and the lines with interplanar distance 0.191 nm vanish.

In the x-ray diffraction pattern of the experimental solid solution with molar content 70% $Ca_2TiSi_2O_8$ and 30% $Sr_2TiSi_2O_8$ splitting of the lines with interplanar distances 0.275 and 0.271 nm and the formation of a new line with the value 0.195 nm are observed.

IR-spectroscopy shows that essentially two regions of the absorption bands with frequencies 400 – 650 and 750 – 1100 cm^{-1} are identified in the spectra obtained for the solid solutions. An appreciable shift of the absorption bands in the direction of lower frequencies and some broadening of the bands occurs from distrontium titanodisilicate to dicalcium

TABLE 1. Physical–Chemical Properties of the Solid Solutions of the System $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$

Compound	Melting temperature, °C	Density, kg/m³	CLTE, 10^{-7} K^{-1}	Refractive indices		Unit-cell parameters, nm	
				N_g	N_p	a	c
$Ca_2TiSi_2O_8$	1420	3110	83.41	2.050	1.961	0.838	0.534
$Ca_{1.8}Sr_{0.2}TiSi_2O_8$	1380	3220	83.62	1.971	1.952	0.790	0.521
$Ca_{1.6}Sr_{0.4}TiSi_2O_8$	1330	3250	83.71	1.943	1.936	0.799	0.520
$Ca_{1.4}Sr_{0.6}TiSi_2O_8$	1300	3270	83.88	1.914	1.908	0.806	0.517
$Ca_{1.2}Sr_{0.8}TiSi_2O_8$	1280	3340	83.95	1.882	1.873	0.810	0.515
$Ca_{1.0}Sr_{1.0}TiSi_2O_8$	1270	3410	84.01	1.841	1.829	0.818	0.511
$Ca_{0.8}Sr_{1.2}TiSi_2O_8$	1340	3490	84.09	1.801	1.801	0.824	0.509
$Ca_{0.6}Sr_{1.4}TiSi_2O_8$	1340	3560	84.24	1.782	1.773	0.831	0.506
$Ca_{0.4}Sr_{1.6}TiSi_2O_8$	1350	3570	84.41	1.775	1.768	0.838	0.504
$Ca_{0.2}Sr_{1.8}TiSi_2O_8$	1370	3610	84.70	1.774	1.752	0.842	0.503
$Sr_2TiSi_2O_8$	1390	3720	84.81	1.764	1.730	0.852	0.493

Fig. 2. Electron-microscopic photograph of a solid solution with molar content 70% $Ca_2TiSi_2O_8$ and 30% $Sr_2TiSi_2O_8$; ×4900.

titanodisilicate in the binary system. The transition from a sample with molar content 20% strontium titanodisilicate to a sample with 30% $Sr_2TiSi_2O_8$ is accompanied by the appearance of an additional absorption band with frequencies near 1250 cm^{-1} and vanishing of the lines belonging to the absorption bands 820 and 900 cm^{-1}.

An electron-microscopic photograph of the equimolar composition of the solid solution is presented in Fig. 2. Tablet-shaped crystals of dicalcium titanodisilicate and plate-shaped distrontium titanodisilicate are clearly visible in the photomicrograph.

CONCLUSIONS

In summary, it was established on the basis of a study of the high-temperature chemical interaction between calcium and strontium titanodisilicates that two limited series of solid solutions in the tetragonal system based on these initial compounds are formed. The regions of the solid solution based on the extreme components of the system extend from 70 to 100% molar content. It was determined that the changes in the density, refractive indices, and unit-cell parameters of the solid solutions as a function of the compositions of the samples are discontinuous.

Glasses and glass ceramic materials were obtained on the basis of studies of the system $Ca_2TiSi_2O_8$–$Sr_2TiSi_2O_8$. The characteristic features of the crystallization of glasses were elucidated and the concentration and temperature ranges of the existence of stable crystalline phases of the obtained solid solutions based on calcium and strontium titanodisilicates were determined.

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